



Stanford University

Advanced Diagnostics of Layered-Oxide Particles

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SLAC National Accelerator Laboratory

Annual Merit Review
DOE Vehicle Technologies Program
Washington, DC
13 June, 2019

Overview

Timeline

- Start Date: Q1 FY18
- End Date: Q4 FY19
- Percent complete: 40%

Budget

- Total project funding: 100% DOE
- FY16 Funding: \$ 450K

Barriers

- Barriers addressed
 - Advanced *in-situ* diagnostic to pinpoint and predict failures in batteries
 - Screen new battery chemistries using advanced diagnostic
 - Electrode lifetime

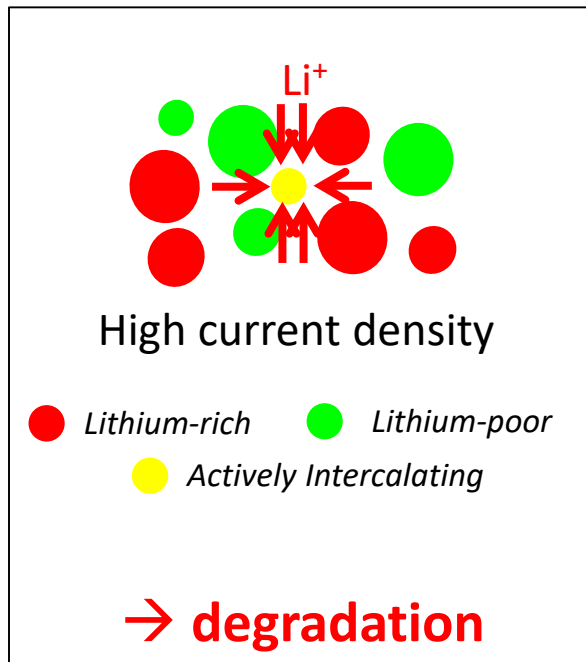
Partners

- Pls: Yi Cui, Will Chueh, Mike Toney
- Collaborators:
 - Gerbrand Ceder (LBNL)
 - Wanli Yang (LBNL ALS)
 - David Prendergast (LBNL TMF)
 - Industry (materials)

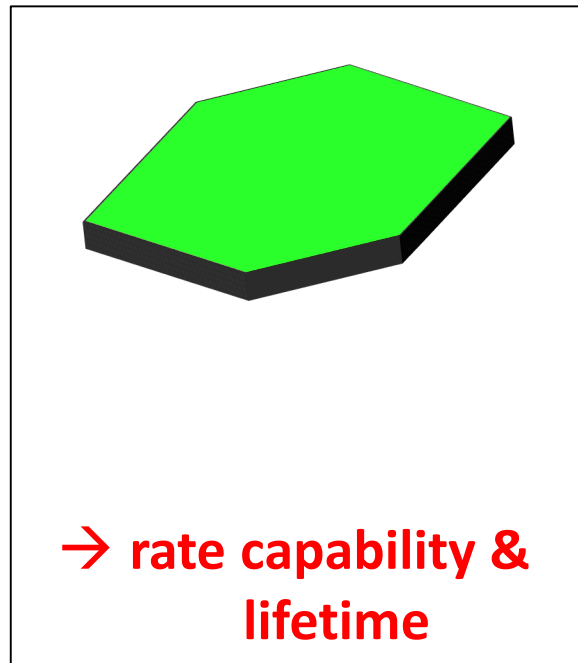
Objectives & Relevance

Objectives: Develop and utilize a correlative microscopy platform to investigate the (de)lithiation dynamics of LMR-NMC and NMC, with the specific goal of understanding factors that determine the rate capability and degradation mechanisms at the secondary particle, single primary particle, and atomistic length scale.

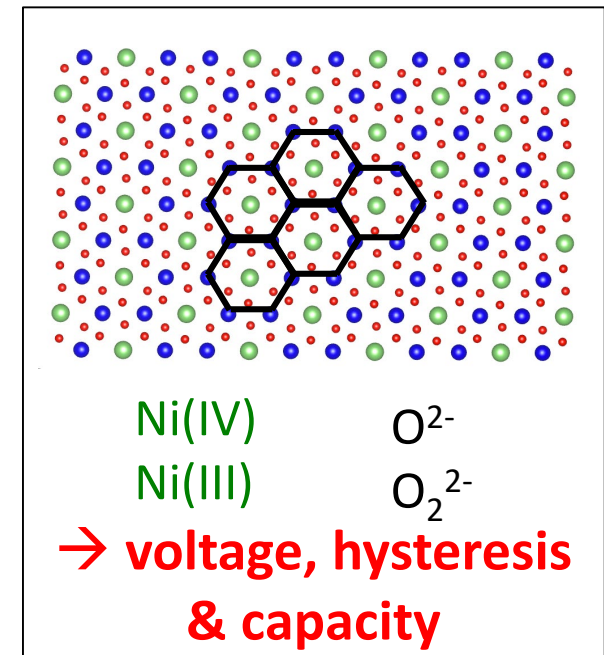
Macroscale: Hot Spots



Mesoscale: Kinetics
& Chemo-mechanics



Atomic: Redox



Objectives & Relevance

Relevance:

- Understand atomistic and mesoscale factors that lead to capacity & voltage fading in layered oxide cathode (LMR-NMC & NMC)
- Develop diagnostic tools that reach new length scales not previously available

Impact:

- Enable accelerated materials development time by understanding capacity & voltage fade mechanisms
- Provide new information to design fast charging protocols and to improve power density

Milestones

FY 2018

- Use of correlative microscopy platform for imaging LMR-NMC and NMC cathode hotspots. (Achieve Q1 2018)
- Spectro-imaging of single NMC particles. (Achieved Q4 2018)

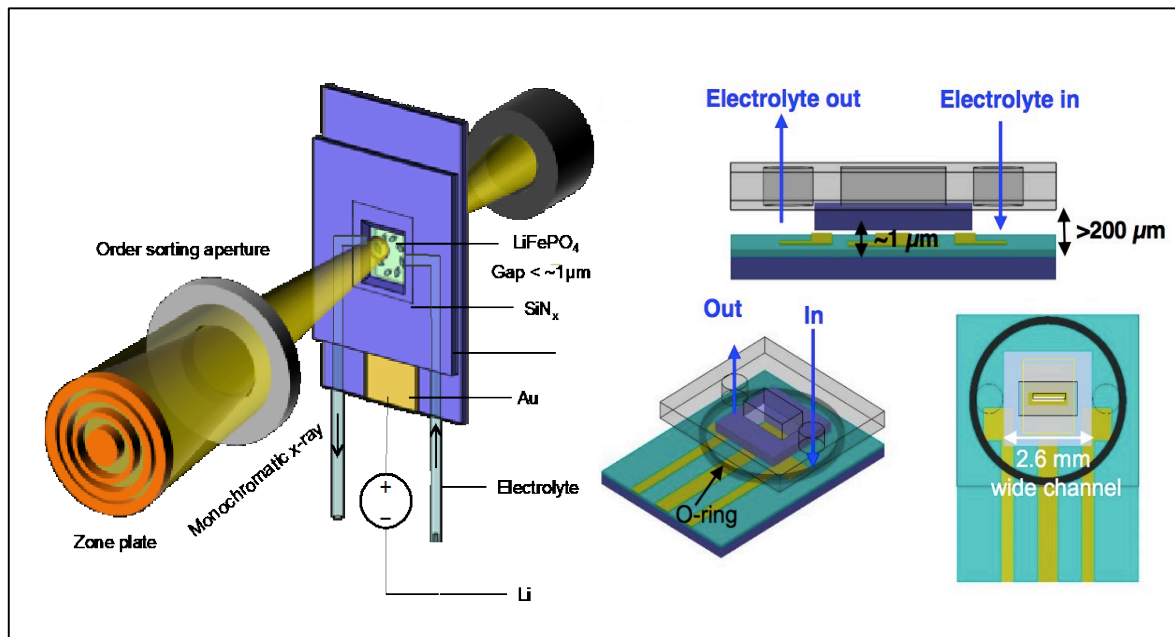
FY 2019

- Quantify the local structure of Li-rich layered oxides using local X-ray probe. (Achieved Q1 2019)
- Assess the effect of synthesis condition of anion redox. (Q4 2019)
- Assess the effect of oxygen vacancies on anion redox. (Q4 2019)

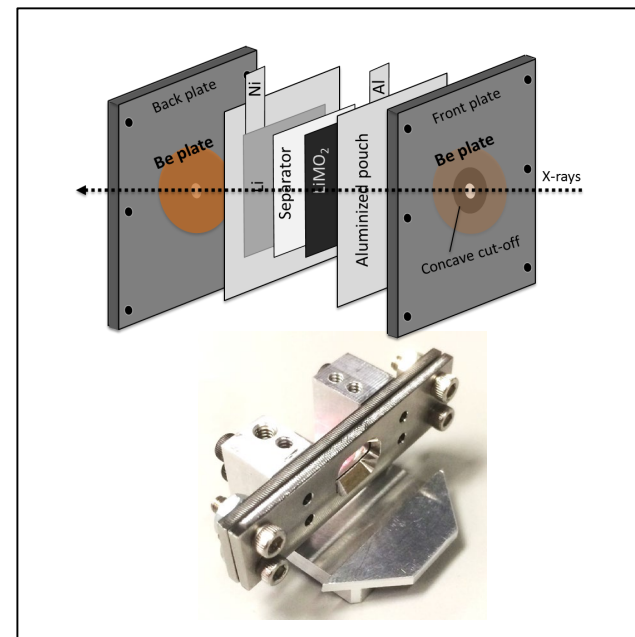
Approach

- Develop & utilize in-situ & ex-situ X-ray spectroscopy, diffraction and microscopy to relate local chemistry, structure and microstructure evolution to battery electrochemical characteristics (voltage, capacity/voltage fade, and activation)
- Correlate with other characterizations such as diffraction & electron microscopy.

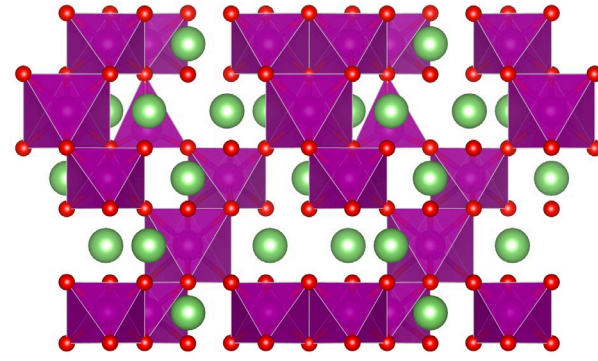
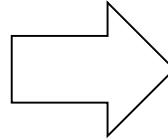
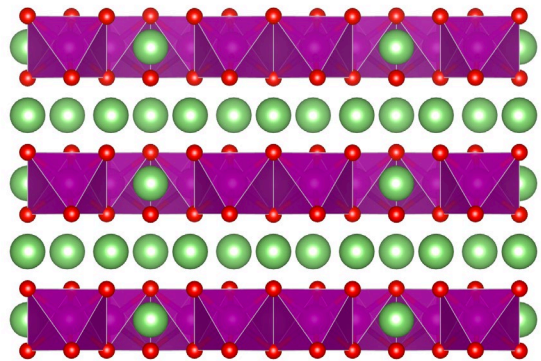
Soft X-ray Spectro-microscopy



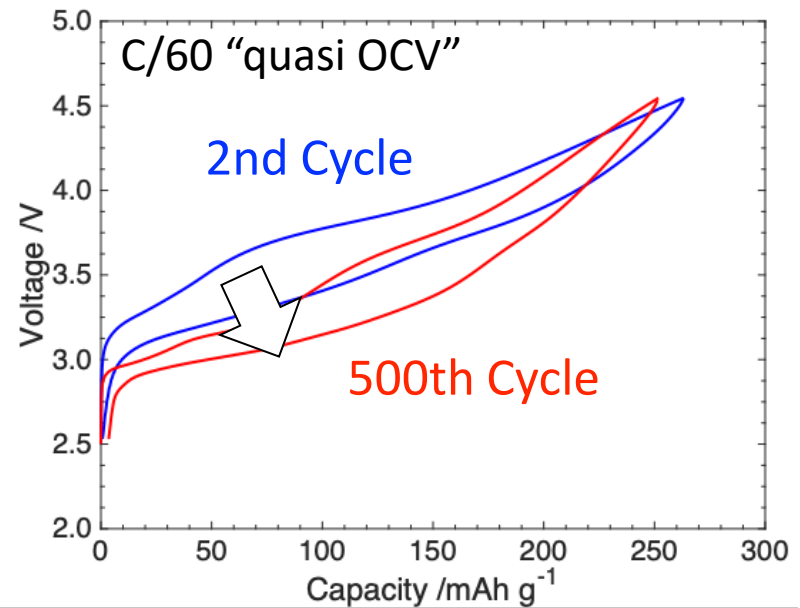
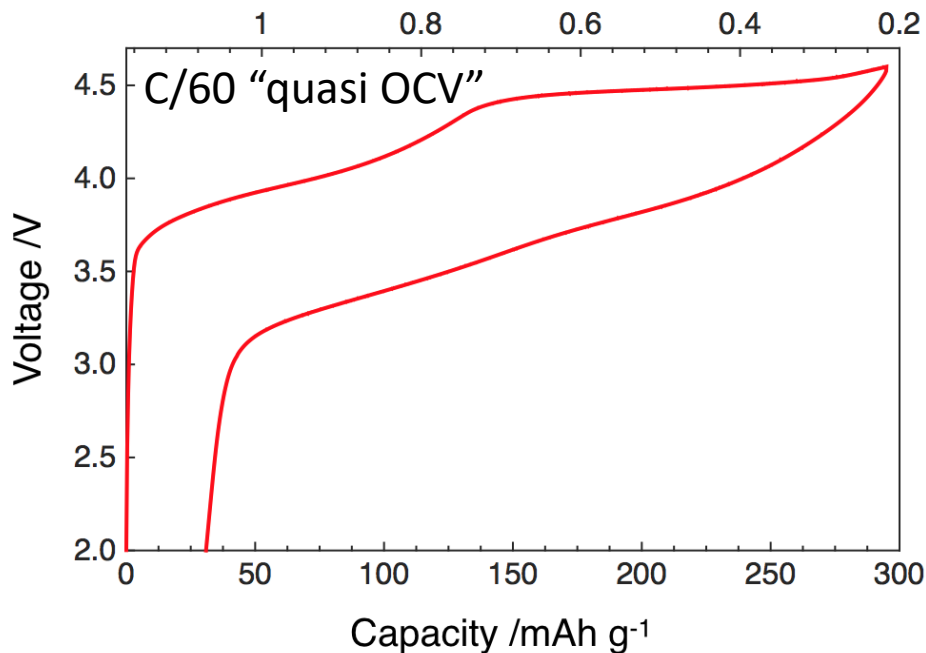
Hard X-ray Diffraction, Spectroscopy & Microscopy



Technical Progress: LMR-NMC redox mechanisms

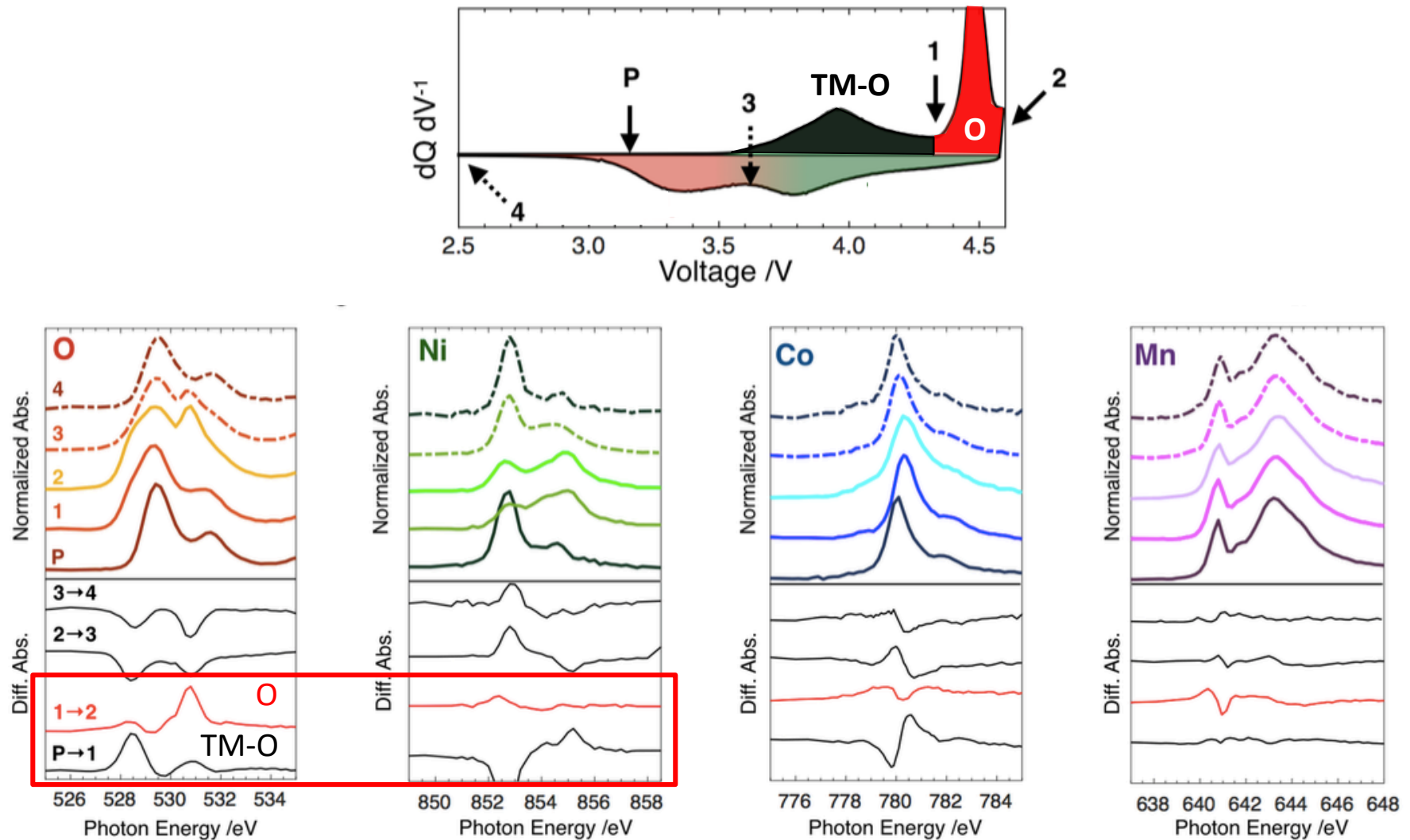


x in $\text{Li}_x\text{Ni}_{0.21}\text{Co}_{0.08}\text{Mn}_{0.54}\text{O}_2$



LMR-NMC and other Li-rich layered oxides exhibit high-voltage substantial capacity which is accompanied by local disordering and voltage fade.

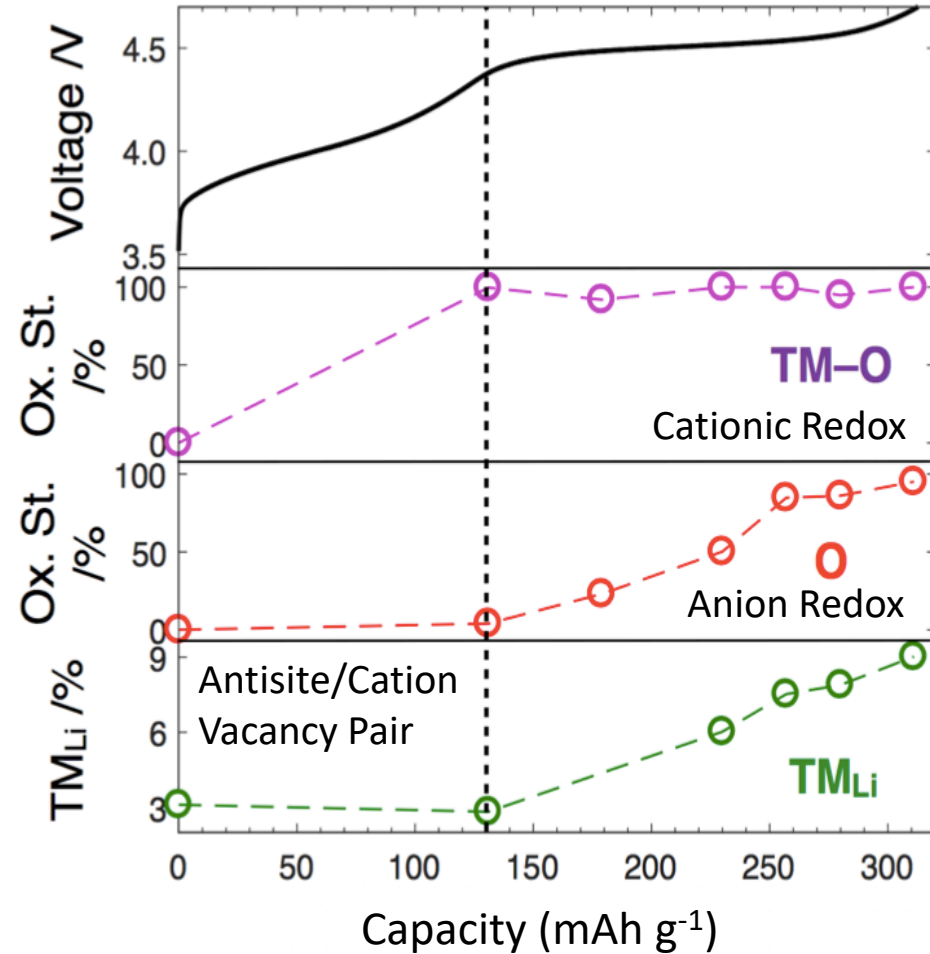
What are the redox centers? Going beyond TMs



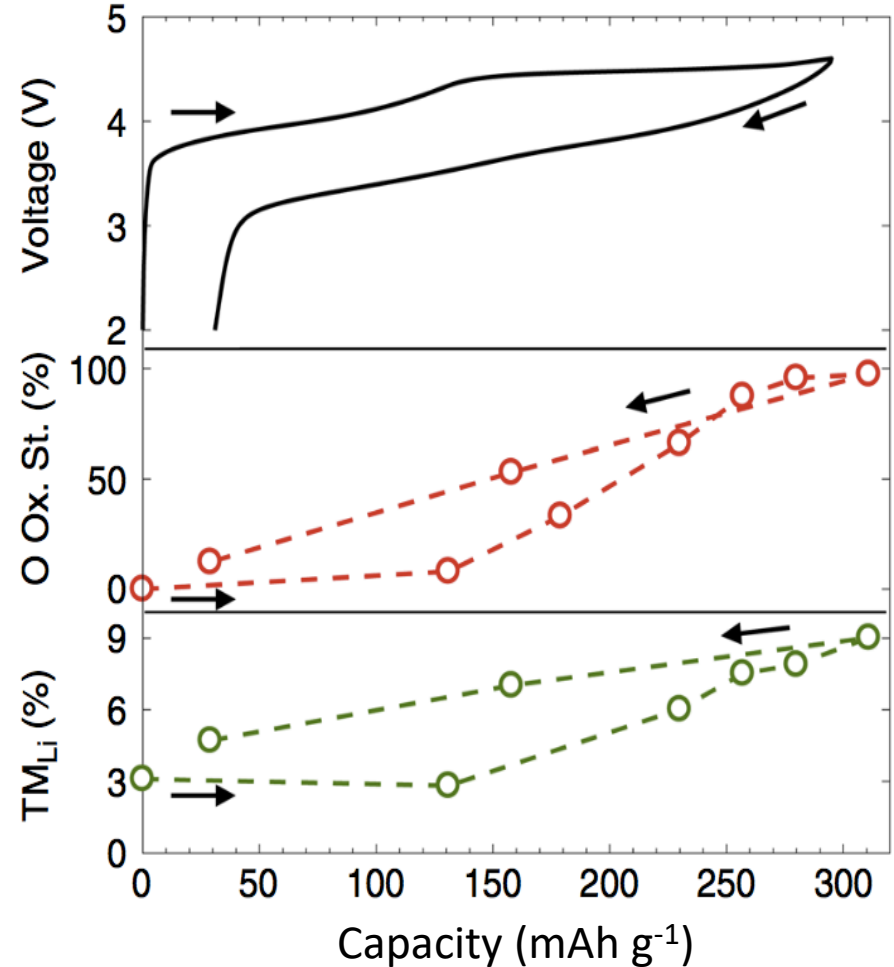
Through soft X-ray spectroscopy, we show that below 4.2V, redox partner upon delithiation is Ni-O (covalent); above 4.2V, the redox partner is essentially pure O (non-bonding).

Coupling between cation migration & anion redox

Cation migration & *plateau*

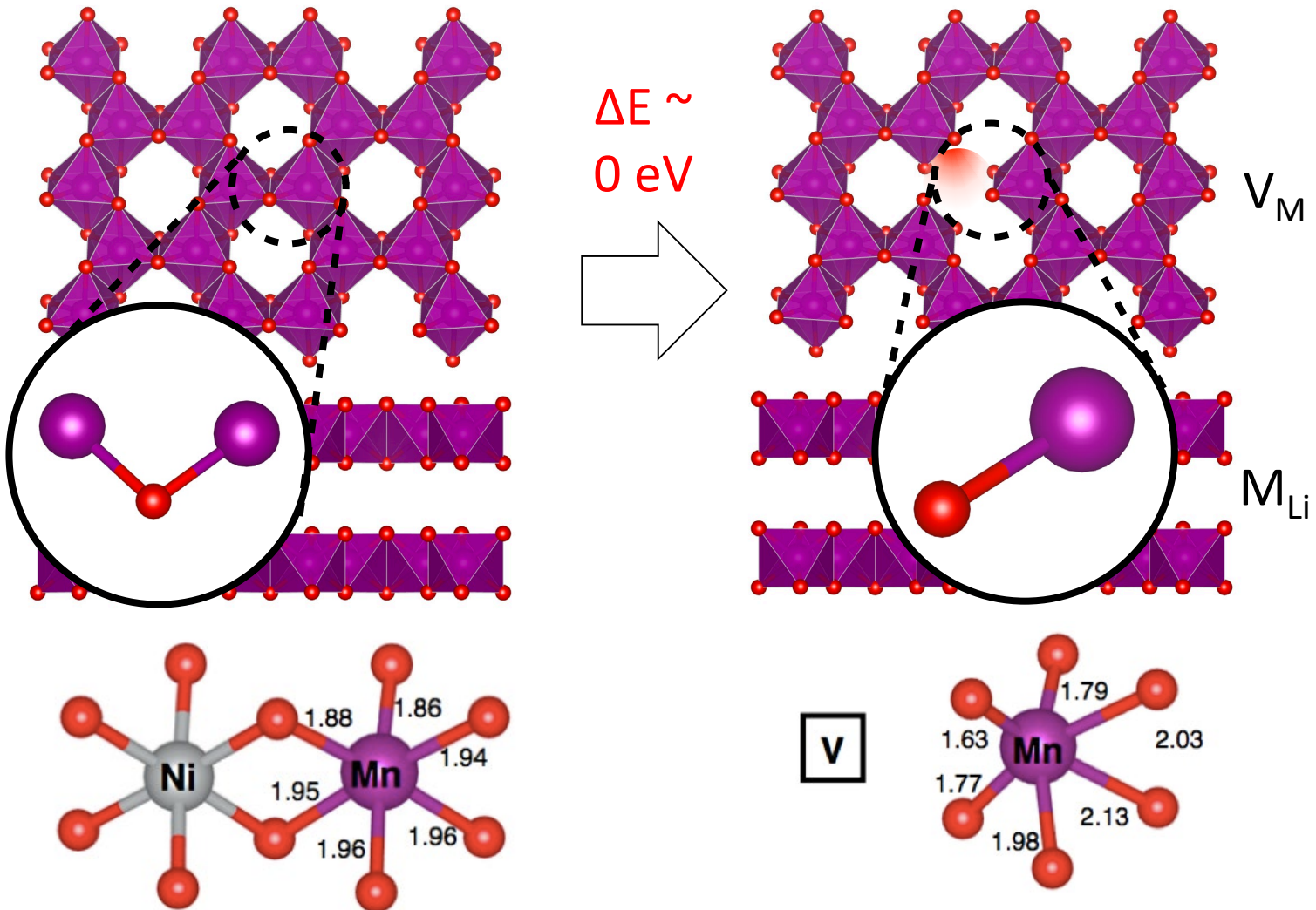


Cation migration & *hysteresis*



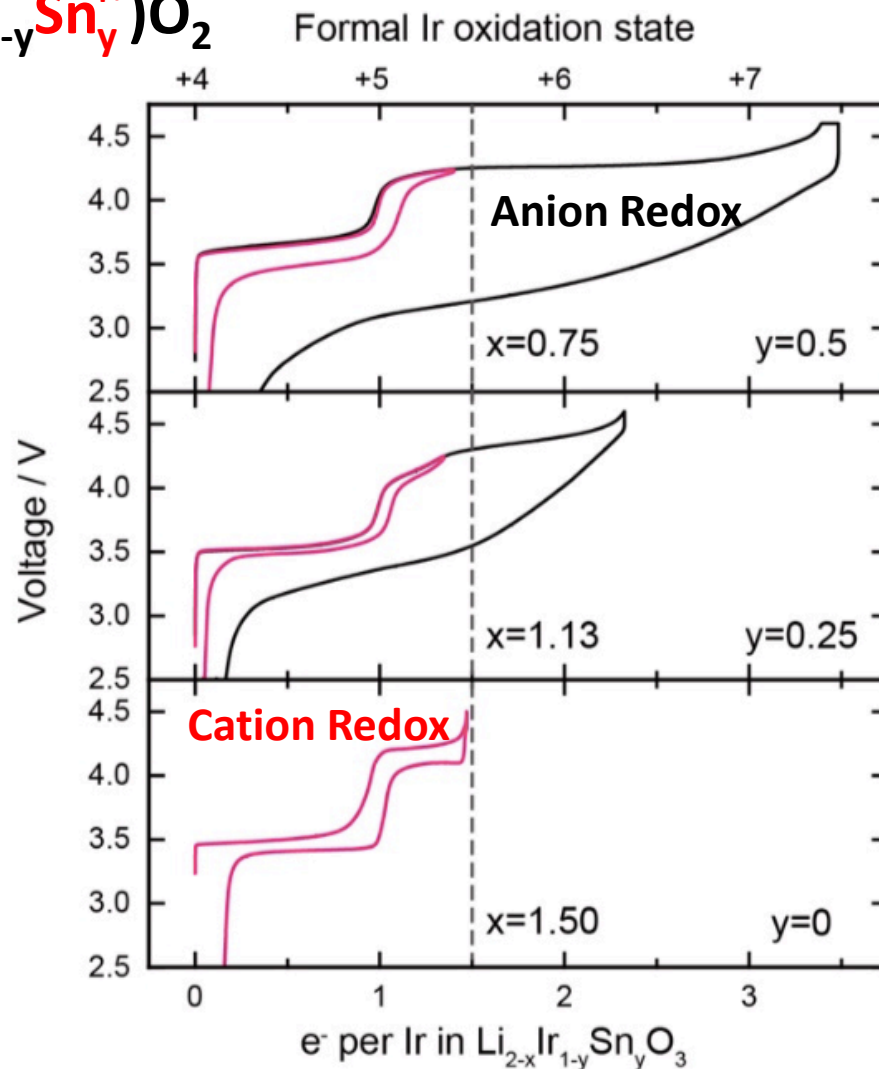
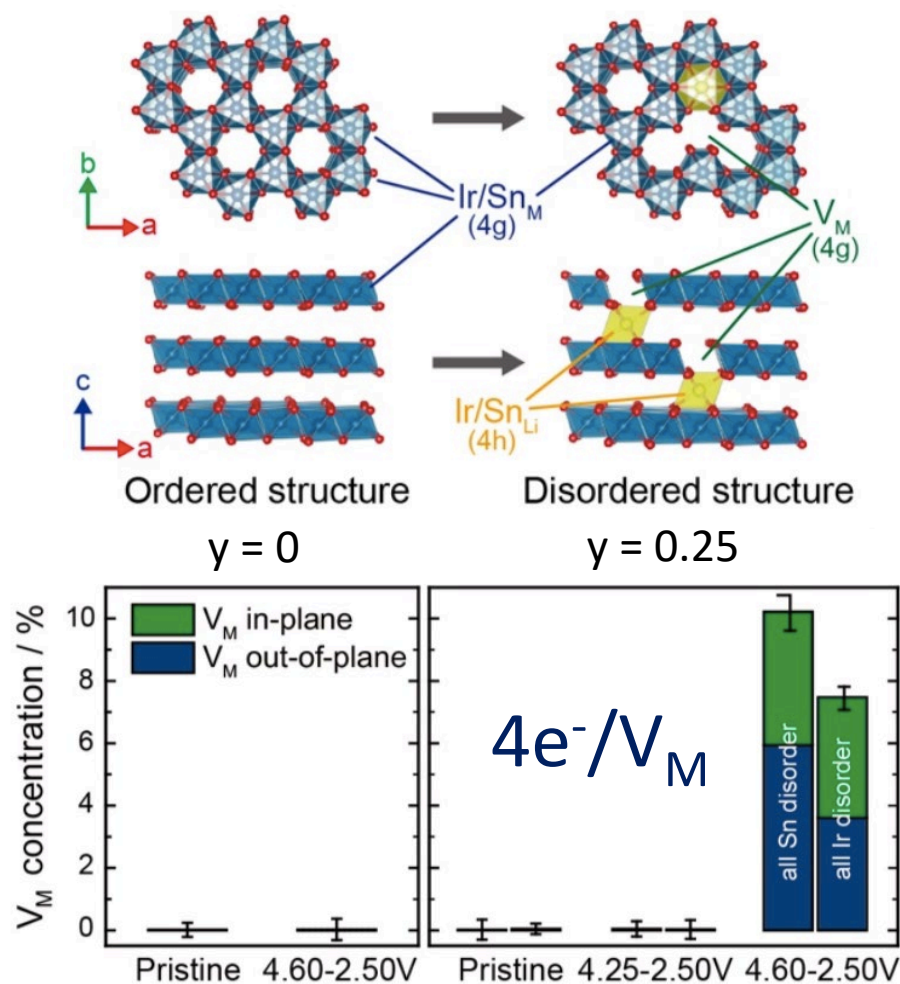
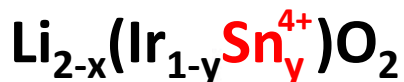
Above 4.2V, the oxygen redox capacity is accompanied by substantial cation migration (i.e., formation of antisite/cation vacancy pair). On discharge, the cations partially migrate back.

Coupling mechanism: *oxygen decoordination*



Upon TM migration, oxygen goes from being bonded to two TM to one TM, effectively generating a TM=O metal oxo species. This process stabilizes the oxygen against evolution and explains why oxygen oxidation and TM migration occur simultaneously.

Turning on/off oxygen decooordination & redox



To confirm the link between metal migration and oxygen redox, iridate model system was explored. Without Sn substitution, there is no metal migration and no oxygen redox. With Sn substitution, oxygen redox occurs and substantial metal migration takes place.

Response to Previous Year Reviewer's Comments

None

Collaboration & Coordination with Other Institutions

Advanced Light Source, LBNL:

- Users facility accessed via proposal (no cost)
- Carry out X-ray microscopy experiments at beam line 11.0.2, 5.3.2
- Carry out resonant inelastic X-ray scattering at beam line 8.0.1

Molecular Foundry, LBNL:

- Users facility accessed via proposal (no cost)
- Carry out density functional theory simulations of lithium-excess layered oxides

Samsung Advanced Institute of Technology

- Materials for NMC and LMR-NMC

Remaining Challenges & Barriers

- Quantify O-O and M-O bond distances in highly disordered cathodes.
- Translate ex-situ experiment to in-situ for both secondary & primary particles
- Couple nanoscale mapping to nanoscale crystallography

Proposed Future Research

- LMR-NMC: quantify anion and cation redox as a function of cycling to fully understand their relationship to capacity and voltage fade
- NMC: connect secondary particle SOC hotspots to stress gradient and preferred particle orientations
- NMC: extend characterization to single particles

Summary

- Developed methods to quantify redox partners at different SOC
- Employed X-ray diffraction to reveal local structure change in LMR-NMC which established how to prevent oxygen evolution at high voltage
- Proposed a decoordination model to explain why oxygen redox occurs simultaneously as metal migration

Acknowledgement

This work was by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, Battery Materials Research Program, U.S. Department of Energy. We grateful acknowledge the guidance from Tien Duong and David Howell.